1911

Scheme for the treatment of copper smelter flue dust

John Perry Walker

Department: Materials Science and Engineering

SCHEME FOR THE TREATMENT

of

COPPER SMELTER FLUE DUST.,

by

John Perry Walker.

A

THESIS

Submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI.

in partial fulfillment of the work required for the

DEGREE OF

BACHELOR OF SCIENCE IN METALLURGY.

Rolla, Mo.

1911.

Approved by D. Copeland

Professor of Metallurgy.

In recent years, methods for improving the prevailing practice in treatment of flue dust have demanded the attention of those engaged in the copper and lead industries. Great advancement has been made in the more complete settling of the dust in large chambers and flues, and in some instances, more particularly in the case of lead smelters, in its extraction from the flue discharge of the furnaces by filtration through bags.

Schemes for re-treating this recovered dust are, however, in a somewhat undeveloped state. Commonly the dust is briquetted and fed to blast furnaces, where the briquettes crumble before sintering can occur, and as high as forty to fifty per cent.may again be blown out with the discharged gases. Another practice at some copper smelters is to charge the dust to reverberatory matte furnaces. These furnaces make little flue dust, wherein lies the advantage over charging to blast furnaces.

In either case, most of the arsenic in the dust is volatilized, recondensing for the greater part in the chambers and flues, some finding its way out into the atmosphere. A minor portion goes into the matte, thereby increasing the troubles of the refiner.

So far as I know, only one plant in the West makes a separation of the arsenic from the flue dust before smelting the latter. This is done by distillation.

The leaching and crystallization scheme, which I propose, should be applicable at works where there is considerable waste heat, and may work out cheaper than the distillation.

While in the employ of a western copper smelter in the year 1904, I discovered that eighty per cent.or more of that portion of the arsenic in the flue dust which was soluble in water, could, by solution, evaporation and sub-

sequent cooling of the solution, be recovered.

This soluble arsenic is probably amorphous or uncrystallized arsenious oxide which is readily soluble in water. The crystallized oxide does not easily dissolve.

Beyond this conception of the character of the soluble arsenic in the flue dust, after considerable research, I came to the conclusion that actual compounds of arsenic with sulphur trioxide are formed, this being more especially true in the case of dust from the roasting furnaces. Whether, after the removal from the flue, these compounds remain intact or break down into amorphous oxide and sulphuric acid, I am not prepared to state. In either case, however, we have another explanation for the ready solubility of the arsenic, besides the assumption of the condensation from flue gases of amorphous oxide.

This idea of the formation of compounds of sulphur trioxide with arsenious oxide may also explain why it is that in some instances the arsenic passes through flues, and out into the atmosphere, while in other instances, under identical conditions of velocity of gases and temperature, there is a more nearly complete settling in the dust. In the one case, suppose the furnace gases discharged contain little or no free sulphur trioxide, then no compounds with arsenic would form. In the other, if there be free sulphur trioxide, this could combine with the arsenic and tend to condense at higher temperatures than arsenious oxide, or the compound meeting with the requisite amount of water vapor at cooler portions of the flue, would break up into sulphuric acid and arsenious oxide. The tenacity with which arsenic is held by sulphuric acid is well known.

For the purpose of determining the practicability of a wet treatment of the flue dust, with a view toward the recovery of arsenic, I carried out the subjoined tabulated experiments and tests. An attempt was made to answer the

following questions:

1. What is best temperature of water to dissolve arsenic?
2. What is time necessary to remove arsenic from dust?
3. What quantity of water is necessary?
4. What amount of evaporation is necessary to remove arsenic?
5. What per cent of arsenic dissolved will crystallize from solution?
6. What time is necessary for crystalization?
7. What is the best method for disposing of final solutions?

By way of solving the first three, preliminary experiments were madd upon small amounts of dust; the remaining questions are worked up by tests upon larger quantities. These more extensive tests are also to be considered in connection with numbers 2 and 3. The copper soluble in water is also taken into account.

15 weighings of 10 gm. each were made into small beakers. Water was added and the mass stirred at intervals through the time specified. Three treatments with water were made in each case.

The manipulation of experiments 1 - 11 inclusive, for the separation of liquid from undissolved material was performed by decanting all liquid upon a filter paper, then washing back into the beaker the small amount of dust which was carried upon the filter by the liquid. Water was then added up to a mark on the beaker for the next treatment and the mass was then heated up to the given temperature. This method of filtering and also the heating of the water with the dust, will explain why the solubility results on experiments 1 - 11 are higher than those on 12 - 15.

The procedure with experiments 12 - 15 was to decant the liquid as closely as possible, and then to the undissolved material in the beaker a measured quantity of water already heated to the temperature given was added.

Per cent.arsenic in dust, 13.36
Per cent arsenic soluble in water, 11.34
Per cent.of total arsenic in dust which is soluble in water, 84.8

	c.c. of water used.	Temperature of water centrigrade.	c.c. of filtrate cold.	Time of first treatment with water - Hours.	Time of second treatment with water.	Time of third treatment with water.	Gm. arsenic per c.c. of filtrate.	Total Gm. arsenic in filtrate.	Per cent.of soluble arsenic dissolved.
No. 1.	62	18	58	0.5	0.5	0.5	0.008221	0.477	42.1
" 2.	62	18	60	1.0	1.0	1.0	0.008367	0.502	44.3
" 3.	62	18	60	1.8	1.8	1.8	0.008524	0.512	45.1
" 4.	62	18	60	2.0	2.0	2.0	0.008758	0.525	46.3
" 5.	90	25	67	0.7	0.7	0.5	0.009540	0.639	56.3
" 6.	90	35	60	0.8	0.7	0.5	0.012355	0.741	65.3
" 7.	90	45	63	1.2	0.7	0.5	0.012121	0.764	67.4
" 8.	90	55	63	1.0	0.7	0.5	0.013372	0.842	74.2
" 9.	90	65	58	1.0	0.7	0.5	0.014858	0.862	76.0
" 10.	90	75	54	0.7	0.7	0.5	0.016578	0.895	78.9
" 11.	90	82	53	0.7	0.7	0.5	0.016422	0.870	76.7
" 12.	114	75	91.5	0.5	0.5	0.5	0.010200	0.933	82.3
" 13.	96	75	72	0.5	0.5	0.5	0.012325	0.887	78.2
" 14.	84	75	59	0.5	0.5	0.5	0.012920	0.762	67.1
" 15.	84	75	60.5	0.5	0.5	0.5	0.014875	0.900	79.9

It will be noted that difference in time does not affect the amount of arsenic dissolved nearly as much as difference in temperature. Comparing No. 2 and No. 4, an hour's difference in time gives a difference of 2% in the arsenic dissolved; whereas, comparing Nos. 4 and 6, an addition of 17 degrees temperature gives an increase of 19% arsenic in one-third the time for the three treatments.

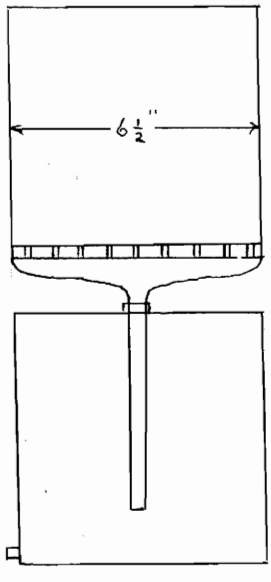
From No. 10, it is shown that 5.7 parts by weight of solution (Specific gravity 1.1) contain 78.9% of the total soluble arsenic in the dust used.

From No. 12, it is shown that 9.5 parts by weight of solution (Specific gravity 1.05) contain 82.7% of the total soluble arsenic.

No. 1 5 shows how the addition of a small amount of sulphuric acid increases the solution of arsenic.

TEST NO. 1.

1000 Gm. of the sample used in the preliminary experiments was placed in a glass percolator for which a false bottom of wood was constructed.



The depth of the dust upon the false bottom was 1-3/4". 1000 c.c. of water at 75 degrees C. placed upon the dust stood at a level of 2¾". Thirteen additions, each of 1000 c.c. of water, were made to the dust, the water being added cautiously to avoid disturbing the bed of dust.

The time required for the water to sink to the level of the dust was noted in the first case. After the second addition of water had leached down, the cold leachings in the receiver were removed and measured, the time of leaching being noted. This was repeated after each succeeding leaching.

It was found that the first 5000 c.c. of leachings contained all but a trace of the soluble copper and 66% of the soluble arsenic. This solution was subsequently evaporated separately from the remainder of the leachings, and is designated in the tabulated report as 1-A, the remainder of the leachings as 1-B.

Upon standing, a yellowish precipitate, in small amount, settled out in the 1-A solution. This was filtered off, weighed and analyzed, and the filtered solution showed no more of this precipitate throughout the course of the evaporation. The weight of the precipitate was 2.061 Gm., and it contained 55.5% arsenic, 20.3% iron and 0.47% copper. This percentage composition does not coincide with that of any known arsenious salt of iron; it may, of course, be a mixture of arsenious oxide with an iron salt, or some basic arsenite of iron. Throughout all the tests, this was the only instance where such a precipitate was obtained. In the tabulated report it is designated "Yellow Precipitate".

The solutions "1-A" and "1-B" were evaporated, the crystals filtered off, weighed and assayed. The crystals contained no trace of iron or copper, but were mixed with some calcium sulphate.

The filtrate from the "1-A" crystals was treated electrolytically for the recovery of the copper. No attempt was made to further eliminate arsenic from the final solution in this case.

For all figures on the results of this test, see Tables 1 (Page 8), 2 (Page 9) and 10 (Page 10).

EXPLANATION OF TABULATED REPORT.

The tables headed "Solubility Results, Arsenic", give the solubility results of the tests.

The sheet headed "Arsenic Elimination", gives results on crystallization of the arsenic and subsequent treatment of filtrates for the further elimination of arsenic.

The results for copper are given in condensed form on the sheet headed "Copper", page No.

Since considerable quantities of solution were used for analysis, the arsenic and copper thus removed from the processes are taken into consideration, and appear in the columns headed "Gm. Removed by Analysis".

The column "Total Gm. Treated", gives the figures resulting from subtracting the amounts of arsenic or copper removed by analysis from the total grammes of arsenic or copper in the dust.

TABLE 1.

SOLUBILITY RESULTS.

A R S E N I C.

	Gm. dust used.	Time of leaching	Gm. As. in dust.	Gm. soluble As. in dust.	c.c. of H_2O used.	Volume of leachings.	Gm. As. dissolved.	Per cent of soluble As. dissolved.	Per cent of total As. dissolved.	Gm. of residue.	Percent of soluble matter in dust.	Gm. As. in residue.	Per cent of total As. left in residue.
		Hr.Min.											
1-A	1000		133.60	113.400									
1st.leach		3 40			1000								
2d. "		3 45			1000	886							
3d. "		1 00			1000	750							
4th. "		1 25			1000	1095							
5th. "		0 40			1000	981							
6th. "		0 50			1000	1070							
Total-A					6000	4782	75.12	66.2	56.2				
1-B													
7th.leach		0 40			1000	900	11.97	10.6					
8th. "		0 40			1000	940	7.78	6.9					
9th. "		0 40			1000	930	5.56	5.0					
10th. "		0 40			1000	850	5.04	4.4					
11th. "		0 40			1000	880	1.49	1.3					
12th. "		0 45			1000	950	0.98	0.9					
13th. "		Not taken			1000	983	0.74	0.6					
Total-B					7000	6433	33.59	29.7	25.1				
Grand Total		15 25	133.60	113.400	13000	11215	108.71	95.9	81.3	545.	45.7	24.445	18.30

								Gm. dust treated.
								Gm. As. dissolved.
								Gm. As. removed by analyses.
								Total Gm. As. treated.
								Weight in Gm.
								Per cent Arsenic.
								Gm. Arsenic recovered.
								Per cent recovery on total As. dissolved.
								Per cent recovery on total As. present.
								Gm. As. removed by analyses.
								Gm. As. recovered on nails.
								Gm. As. recovered otherwise.
								Per Cent of total As. in dust removed.
								Per cent of total As. dissolved recovered.
								Gm. As. in final liquid.

Orr's Gels

Arsenic Trioxide.

Yellow Precipitate.

March 7.

TABLE 10.

COPPER.

	Test No. 1	" " 2	" " 3	" " 4	" " 5
Gm. dust used.	1000	250	250	1000	750
Gm. Cu. in dust.	62.200	15.550	15.100	60.400	45.300
Gm. Cu. dissolved.	40.000	10.000	9.720	39.081	29.396
Gm. Cu. removed by analyses.	0.400	0.372	0.097	0.433	0.336
Gm. Cu. in solution Electrolyzed.	39.600	-	-	38.648	29.560
Total Gm. Cu. operated on after taking assay samples.	31.800	15.176	-	59.967	44.964
Gm. Cu. recovered by electrolysis.	30.354	-	-	35.763	25.311
Gm. Cu. recovered on nails.	-	9.628	9.623	2.385	4.249
Gm. Cu. in residue.	22.208	-	-	-	-
Per cent of total Cu. left in residue.	35.7	-	-	-	-
Per cent of total Cu. in dust removed.	64.30	65.80	63.00	64.40	65.70
Per cent of total dissolved Cu. recovered.	91.80	100.00	100.00	100.00	100.00
Gm. Cu. in final solution.	3.246	none	none	none	none

TEST NO. 2.

250 grammes of the same sample used in Test No. 1, were treated with water in a beaker of 1000 c.c. capacity. The mass was stirred three times at intervals of 15 minutes and allowed to settle, which occurred in 10 minutes in the case of the first treatment with water; in less time with the others. Six treatments with water were made. The filtrate from each treatment was measured as in the case of No. 1 Test.

All filtrates were, however, combined for the crystalization. The filtrate from the crystals was treated with iron nails for the recovery of the copper. It was discovered here that by heating, not only all copper, but all arsenic was precipitated by the iron. If the treatment is cold, the copper is precipitated more slowly, but arsenic cannot be precipitated completely in a number of days.

For figures, see Tables 3 (Page 12) and 4 (Page 13).

TEST NO. 3.

A different sample of dust was used here. 250 grammes of dust were treated by agitation as in Test No. 2. The dust received five different washings with varying quantities of water; but to the water used in the first washing were added 10 c.c. of sulphuric acid. The filtrates were all united and evaporated; the crystals filtered out, and the remaining solution treated with nails without heating.

For figures, see Tables 3 (Page 12), 4 (Page 13) and 5 (Page 14).

TABLE 3.

SOLUBILITY STUDIES.

ARSENIC.

	Gm. dust used.	Time of Leaching.	Gm. As. in dust.	Gm. Soluble As. in dust.	c.c. of H_2O used.	Volume of leachings.	Gm. As. dissolved.	Per cent of soluble As. dissolved.	Per cent of total As. dissolved.
Test 2	250		34.4	28.350	700	464	13.36	47.1	
1st.wash					500	510	6.92	24.4	
2d. "					400	426	3.42	12.0	
3d. "					500	296	1.23	4.3	
4th "					250	237	0.57	2.0	
5th "					250	283	0.43	1.5	
6th "					2400	2218	25.93	91.3	75.3
Total			34.4	28.350	2400	2009	25.76	58.5	68.3
Test 3.	250		39.20	33.125	2410	2000	26.76	58.5	68.3

	Gm. of residue.	Per cent of soluble matter in dust.	Gm. As. in residue.	Per cent of total As. left in residue.
Test 2	139.	44.2		
Test 3.	143.	45.7		

TABLE 4.

ARSENIC ELIMINATION.

No. 3	No. 2	
250	250	Gm. dust treated.
24.73	25.93	Gm. As. dissolved.
0.57	0.96	Gm. As. removed by analyses.
25.30	26.41	Total Gm. As. treated.
20.89	20.94	Weight in Gm.
71.6	69.0	Per cent Arsenic.
20.37	19.97	Gm. Arsenic recovered.
76.7	80.0	Per cent recovery on total As. dissolved.
51.3	59.7	Per cent recovery on total As. present.
		Gm. As. removed by analyses.
3.59	4.93	Gm. As. recovered on nails.
		Gm. As. recovered otherwise.
61.5	71.4	Per cent of total As. in dust removed.
90.3	100.0	Per cent of total As. dissolved recovered.
2.56	none	Gm. As. in final liquid.

TABLE NO. 5.

Water used for Treatment.

Tests 3, 4 and 5.

1st	Treatment (Tests 3, 4-A, 5-A)	1000 c.c.
2d.	"	500 "
3d	"	500 "
4th	"	200 "
5th	"	200 "

First Treatment of 4 (B, C and D) and 5 (B and C) was with final solution from 4-A and 5-A, respectively.

----o----

TABLE NO. 11.

E V A P O R A T I O N .

Test No.	1-A,	From	4782	c.c. to	600	c.c.
" "	1-B,	"	6358	" "	355	"
" "	2	"	2098	" "	170	"
" "	3	"	1880	" "	155	"
" "	4-A	"	1880	" "	120	"
" "	4-B	"	1885	" "	200	"
" "	4-C	"	1885	" "	200	"
" "	4-D	"	1880	" "	200	"
" "	5-A	"	1880	" "	120	"
" "	5-B	"	1997	" "	255	"
" "	5-C	"	1997	" "	200	"

TEST NO. 4.

250 grammes were treated by agitation as in Test No. 2. The dust was washed five times with varying quantities of water, but no acid was used. The filtrate from the crystals was electrolyzed for the recovery of copper, and the final solution was diluted to 1000 c.c. with water and used over again as a solvent for 250 grammes more of the dust. After removing the crystals, this second solution was electrolyzed for copper as before.

The final solution from the second 250 grammes was again used upon 250 grammes more of dust, repeating the same operation as before. And again the final solution from the third 250 grammes was used upon a fourth weighing of 250 grammes.

The solution remaining after electrolysis, in the case of this fourth treatment of dust, was freed from all remaining copper and a portion of the remaining arsenic by precipitation on nails.

These four separate treatments each of 250 grammes of dust, are designated "4-A", "4-B", "4-C" and "4-D".

The evaporation of No. 4-D solution proceeded so far that considerable salt other than arsenious oxide settled out. (It will be noted that all the soluble iron of the entire 1000 grammes of dust was accumulated here). It was supposed that this other material was a basic salt which would require more acid to dissolve it, consequently 10 c.c. of sulphuric acid and 200 of water were added. This failing to dissolve the iron, 400 c.c. more of water were added, whereupon the precipitated salt almost immediately went into solution. This would indicate that it was, for the most part, a normal

salt and would not have precipitated had not the evaporation been carried so far. After this dilution, the liquid was again evaporated to 400 c.c. before filtering off the crystals. (In explanation, I will state that the evaporation of these large quantities of solution in large dishes, required considerable heating surfact, a nd it would have interfered with the work of others to appropriate this space in the day-time. As a result the evaporations were allowed to proceed over night in the laboratory dryer. By this means, the conclusion of these tests, which involved a considerable length of time, were greatly expedited, although the regulation of evaporations could not be attended to so well as desired.)

For figures, see Tables 6 (page 17), 7 (Page 18) and 10 (Page 10).

TABLE 6.

SOLUBILITY RESULTS.

ARSENIC.

Test	Gm. dust used.	Gm. As. in dust.	Gm. Soluble As. in dust.	c.c. of H_2O used.	Volume of leachings.	Gm. As. dissolved.	Per cent. of soluble As. dissolved.	Per cent of total As. dissolved.	Gm. of residue.	Per cent. soluble matter in dust.	Gm. As. in residue.	Per cent. of total As. left in residue.
A	250	59.20	55.125	2400	2400	23.11	69.7	59.0	150.	44.0	9.330	35.90
B	250	59.20	55.125	2250	2250	27.56	82.2	70.3	145.			
C	250	59.20	53.125	2200	2200	27.09	81.8	69.1	137.			
D	250	59.20	53.125	2200	2200	29.82	90.0	76.1	140.			
Total.		156.80	132.500	9030	6010	107.60	81.2	68.6	570.	45.0		

TABLE 7.

ARSENIC ELIMINATION.

	Gm. dust treated.	Gm. As. dissolved.	Gm. As. removed by analyses.	Total Gm. As. treated.	Crystals. Weight in Gm.	Per cent Arsenic	Gm. Arsenic recovered.	Per cent recovery on total As. dissolved.	Per cent recovery on total As. present.	Gm. As. removed by analyses.	Gm. As. Recovered on walls.	Gm. As. recovered otherwise.	Per cent of total As. in dust removed.	Per cent of total As. dissolved recovered.	Gm. As. in final liquid.
No. 4-A	250	23.11	0.23		25.68	72.7	18.63								
" B	250	27.56	0.32		32.65	72.2	23.72								
" C	250	27.09	0.35		31.20	71.8	22.42								
" D	250	29.82	0.42		32.73	72.3	23.65			0.71	5.25				11.91
Total		107.60	1.32	155.48	122.46	72.2	88.42	83.2	56.8	0.71	5.25		60.5	88.4	11.91

TEST NO. 5.

This test was similar in most respects to No. 4. Three, instead of four, successive weighings of 250 grammes of dust were treated, the final solution from the first weighing being used over for the leaching of the second weighing, and the final solution from the second for the leaching of the third. Each weighing of dust received five washings, but to the water used in the second washing of the first 250 grammes of dust, was added 10 c.c. of sulphuric acid.

The final solution from the three treatments was treated with nails as in the case of Test 4. The three treatments are designated, "5-A", "5-B" and "5-C".

After separation of the undissolved nails, and precipitated arsenic and copper, portions of the remaining solution were treated with slaked lime to determine what could be done for the further elimination of arsenic.

It was found that 98 grammes of lime would neutralize the solution and precipitate 7.775 grammes of arsenic and 4.440 grammes of iron. Upon treating the precipitate with a slight excess of sulphuric acid and filtering, the filtrate contained 3.350 grammes of lime.

To dispose of such a precipitate as the above, it might be added to the dust prior to leaching. The acid liquor from a previous treatment of dust would dissolve the arsenic and iron and at the same time a portion of the lime, most of the precipitated lime remaining with the tails as calcium sulphate.

Some experiments were made by adding lime directly to a solution from which the arsenic had been crystalized as far as possible. This, however, produces a voluminous precipitate of ferrous and ferric hydroxides, cuprous hydroxide, and basic ferric arsenite with possibly calcium arsenite, and what to do with such a precipitate was not known.

In the use of lime in Test 5, care was taken to use no more than necessary to neutralize the solution, thus avoiding the precipitation of a large amount of iron. By using more lime all arsenic could have been precipitated, but with it considerably more iron and lime.

After treating a solution with nails, the iron in solution is reduced and when lime is added to this reduced solution not nearly so much iron is precipitated asswould be were the solution in a partially oxidized state. The excess of free acid is also taken up by the metallic iron.

For figures on test 5, see Tables 8 (Page 21), 9 (Page 22) and 10 (Page 10).

TABLE 8.

SOLUBILITY RESULTS.

ARSENIC.

	Gm. dust used.	Gm. As. in dust.	Gm. soluble As. in dust.	c.c. of H_2O used.	Volume of leachings.	Gm. As. dissolved.	Per cent of soluble As. dissolved.	Percent of total As. dissolved.	Gm. of residue.	Per cent of soluble matter in dust.	Gm. As. in residue.	Per cent of total As. left in residue.
Test 5-A	250	39.20	33.125	2400	2000	26.04	78.6	66.4	144.			
B	250	39.20	33.125	2017	2795	27.95	84.3	71.3	140.			
C	250	39.20	33.125	2145	2017	32.23	97.3	77.1	134.	46.4	6.968	22.90
Total.		117.60	99.375	6825	6054	86.22	86.8	73.3	418.	44.0		

TAILS FROM 5 - C.

Insoluble	69.4%
S.	2.9
Fe.	8.7
As.	5.2
Cu.	3.63

TABLE 9.

ARSENIC ELIMINATION.

	Gm. dust treated.	Gm. As. dissolved.	Gm. As. removed by analyses.	Total Gm. As. treated.	Crystals. Weight in Gm.	Per cent arsenic.	Gm. arsenic recovered.	Per cent recovery on total As. dissolved.	Per cent recovery on total As. present.	Gm. As. removed by analyses.	Gm. As. recovered on nails.	Gm. As. recovered otherwise.	Per cent of total As. in dust removed.	Per cent of total As. dissolved recovered.	Gm. As. in final liquid.
No. 5-A	250	26.04	0.26		26.76	72.5	19.40					by lime			
" B	250	27.95	0.34		33.14	72.0	23.86								
" C	250	32.23	0.42		35.45	72.5	25.70			0.65	7.78	7.144			0.67
Total.		86.22	1.03	116.57	95.35	72.3	68.96	80.9	50.9	0.65	7.78	7.144	72.3	99.2	0.67

C O N C L U S I O N S.

1. Best temperature of water to dissolve arsenic.

Actually boiling the dust with water accomplishes the purpose most readily; but in these tests the water and cup was 80 degrees C., that being the temperature attainable inman open vessel with the heating aparatus of this laboratory.

2. Time necessary to remove arsenic from dust.

The soluble arsenic of the dust goes into solution quite rapidly.

If an agitation and siphoning process be used, it would be advisable to stir until the solution had cooled down considerably, then settle and remove the solution with a floating siphon. Settling is rapid since the constituents of the dust which are dissolved, are the finely divided particles, and the residue remaining consisting of the coarser particles of higher specific gravity, such as insoluble silicates and raw sulphide, which do not remain suspended in the liquid. Referring to the sheet on solubility, it will be observed in the case of test No. 2, that the first washing dissolved 47% of the soluble arsenic of the dust; the residue settled completely in ten minutes, as stated in the written description of Test No. 2. With the subsequest washings, settling resulted in about five minutes. This question of settling might be determined more definitely, if deemed necessary, but comparatively speaking, the material is an ideal one so far as this question is concerned. The arsenic dissolves rapidly and the undissolved material settles rapidly leaving the supernatunt liquid clear except at the immediate surface where a scum of undissolved matter is held. A floating siphon dipping just under the surface would probably deliver a solution requiring no filliation.

As a result of Test No. 1, it would appear that leaching with a tank of false bottom would be practicable, although the first leaching proceeds slowly, the subsequent ones become much more rapid, as the finely divided soluble material is eliminated. The first leaching would, no doubt, have proceeded more rapidly had a larger quantity of water been used.

3. What is the quantity of water necessary?

In Test No. 1, 8.8 parts by weight of water obtained 93.7% of the total soluble arsenic in the dust. The resulting solution had a specific gravity of 1.05. In Test No. 2, 9.2 parts by weight recovered 91.3% of the soluble arsenic. In Test No. 3, 8.4 parts by weight of water obtained 88.3 %. In Test No. 4, 8.4 parts by weight of water recovered 81.2 % of the soluble arsenic. In Test No. 5, 8.4 parts by weight of water obtained 86.8 % of the soluble arsenic.

To sum up, for a given quantity of water, leaching gives a better extraction than agitation and decantation. ~~Note in different conditions.~~

The addition of a small quantity of acid increases the extraction, and the use of the final solution from one leaching for the leaching of another dust also increases the extraction.

4. Amount of evaporation necessary to crystalize arsenic.

In Test No. 4, the best crystalization of arsenic was obtained when about 90% of the entire amount of solution was evaporated. The evaporation of solution "D", Test 5, was, however, further than necessary, the evaporation of 80% of the solution being sufficient. (See Table 11, page 14).

5. What per cent of arsenic can be crystallized out?

83 per cent of the arsenic dissolved was crystallized out in Test No. 4. This indicates another advantage of using final solutions over again for leaching.

6. What is the time necessary to crystallize the arsenic?

This depends upon the rate of evaporation, which again depends upon the temperature, the draft above the liquid undergoing evaporation, and the area of surface exposed. The evaporation of water at 80 degrees C. under the laboratory hood was found to be 959 c.c. for each square foot of liquid surface per hour. As an illustration, if we assume an evaporating tank 10' x 20', there would be an evaporation of 4603 liters in 24 hours, which, assuming 80 per cent as the desirable evaporation, would dispose of 5754 liters of solution. These 5754 liters of solution would represent 677 Kilos or 1489 lbs. of dust treated, assuming 8.5 parts by weight of solution to each part by weight of dust. This evaporation figure is the result of determining the evaporation from two vessels, one of 4" diameter, the other of $6\frac{1}{2}$". Although the two determinations checked, whatever error there is in the figure found, would be greatly multiplied in such a calculation as that of the illustration. The figure for the dust disposed of may either be too high or too low.

7. Method of rendering final solution harmless.

Test 2 illustrates that it is possible after crystallization to throw out all remaining arsenic as well as copper by heating with iron. The arsenic is precipitated as metallic arsenic with the metallic copper. This arsenic readily roasts off as arsenious oxide when heated in the presence of

air. In case of a final distillation of the crystals, this metallic arsenic and copper might be treated with the crystals.

If all arsenic be not removed by iron, the final solution can be treated with lime. The resulting precipitate could be added to another dust and the whole leached with the acid liquid remaining after electrolysis of other solutions. The leachings would contain some lime which would settle out as sulphate in subsequent crystallization. Or the precipitate could be added to leachings undergoing evaporation, whereupon more calcium sulphate would be obtained with the crystals than in the case of adding the precipitate to the dust, but in case of a final distillation the calcium sulphate would not distill and possibly some use could be made of it.

In case a final solution containing a small quantity of arsenic and free acid and a large quantity of iron were run into the river, possibly there is sufficient lime in the river to neutralize the slight remaining acidity and allow of the precipitation of the arsenic as ferric arsenic, or calcium arsenite. This, taken in conjunction with the proportion of arsenic in a final solution to the volume of water into which it would be run, seems to obviate the necessity of removing every trace of arsenic from a solution.

From the standpoint of the tests, it would appear advisable to recover most of the copper electrolytically. (85 to 90 per cent was thus recovered in Tests 4 and 5. If this be done considerable sulphuric acid is liberated and the solution remaining can be used for subsequent leachings. By using these solutions over again less water is required and a greater saving of crystals results.

The crystals in tests 1 and 2 were mixed with some calcium sulphate.

Those in the other tests contained no lime, but did contain fractions of a per cent of copper and iron and this could have been improved by further washing. About 45 per cent by weight of these dust samples was soluble in water.

The following Flow Sheet indicates a process whereby all arsenic would be eliminated. (See page 28).

PROPOSED FLOW SHEET.